

N-benzyl-4-aminophenol derivs. as oxidn. dye developers - for human hair, giving strong, bright shades of good fastness**Publication number:** DE4200534**Publication date:** 1993-07-15**Inventor:** KONRAD GUENTHER DR (DE); KNUEBEL GEORG DR (DE); HOFFKES HORST DR (DE); LIESKE EDGAR (DE)**Applicant:** HENKEL KGAA (DE)**Classification:****- International:** C07C215/76; C07C217/58; C07C215/00; C07C217/00; (IPC1-7): A61K7/13; C07C215/76; C07C217/58; D06P1/32; D06P3/08**- European:** A61K7/13D; C07C215/76; C07C217/58**Application number:** DE19924200534 19920111**Priority number(s):** DE19924200534 19920111**Report a data error here****Abstract of DE4200534**

Use of N-benzylamino-phenols of formula (I) or their salts as precursors in oxidn. dyeing is new. Where R¹-R⁷ = H or 1-4C alkyl; up to 3 of R³-R⁷ can also be Cl or OR⁸ and the other R gps. H; R⁸ = H, 1-4C alkyl or 2-4C hydroxyalkyl. (I) and their salts are new where (a) R³ = R⁵ = H; (b) R³, R⁵ and R⁷ = 1-4C alkoxy; (c) R⁴, R⁵ and R⁶ = 1-4C alkoxy; or (d) R⁴ and R⁶ = 1-4C alkoxy and R⁵ = OH, th eother R gps. being H. Pref. deriv. of (I) is N-(2,4-dihydroxybenzyl)-4-aminophenol. USE/ADVANTAGE - (I) are developers for dyeing keratin fibres, esp. human hair. When used with a wide variety of usual couplers they provide bright shades (beige to brown-violet) of good fastness properties. Partic. they give shades of better brightness, colour depth and light fastness than 4-aminophenol itself.

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Result Page

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The subject of the invention is the use of N-Benzylaminophenolderivaten as developer components in oxidation coloring means.

For coloring hair the so-called oxidation hair coloring means play a preferential role because of their intensive colors and good authenticity characteristics. Such hair coloring means contain oxidation coloring material before products in a cosmetic carrier. As oxidation coloring material before products Entwicklersonstanz and Kupplersonstanz are used. The developer components train the actual coloring materials under the influence of oxidizing agents or of atmospheric oxygen among themselves or under clutch with one or more Kupplersonstanz.

A certain Entwicklersonstanz can form also very different color nuance by combination with different Kupplerson. Nevertheless often does not succeed coming with the help of only one Entwicklersonstanz to the variety of natural hair color nuances. In practice therefore usually a combination of different developer components and Kupplersonstanz is necessary, only one, to receive natural-working hair colouring. Therefore need of new developer components constantly exists.

Good oxidation coloring material before products must fulfill primarily the following conditions: They must train the desired color nuances with the oxidative clutch in sufficient intensity and authenticity. Furthermore they must possess a good absorptive power on human hair, whereby no noticeable differences between strained and freshly regenerated hair may exist. They should be steady against light, warmth and the influence of chemical reducing agents, z. B. against continuous waving liquids. Finally they are not to anfärben the scalp too much, and above all they are to be harmless in toxicological and dermatologischer regard.

As Entwicklersonstanz usually primary aromatic amines with a further are used in Para or Orthoposition free or substituted hydraulic XY or amino group, furthermore Diaminopyridinderivate present, hetero-cyclic Hydrazonderivate or 4 - Aminopyrazolonderivate. As so-called Kupplersonstanz Methaphenylendiaminderivate, Naphthole, Resorcinderivate and Pyrazolone are used.

4-Aminophenol is for a long time well-known as developer component for oxidation hair coloring means. It was now found that dur the use of N-benzylierten 4-Aminophenolen as developer component in oxidation hair coloring means the hair colouring hinsichtlic color brilliance, coloring intensity and light fastness be improved clearly can.

The subject of the invention is the use of N-Benzylaminophenolen of the formula I

EM13.1
where R< 1> to R< 7> hydrogen or alkyl groups with 1-4 C-atoms is independent and up to three of the groups R< 3> to R< 7> also chlorine or a group of OR< 8> and the remaining hydrogen are, whereby R< 8> Hydrogen, an alkyl group with 1-4 C-atoms or a group of hydroxyalkyls with 2-4 C-atoms is, or their salts as developer component in oxidation coloring means with a content of usual Kupplersonstanz to the colouring of Keratinfasern, in particular from human hair.

The N-Benzylaminophenole of the formula I is oxidation coloring material before products of the type of the Entwicklersonstanz, D. h. they are able to train coloring materials under the effect of oxidizing agents. In presence of Kupplersonstanz however particularly brilliant and intensive colors are formed. As Kupplersonstanz are suitable above all the m-Phenylendiamine, m-Aminophenole, Resorcine, Naphthol-1, 1.5 - and 2.7 - Dihydroxynaphthalin, hydraulic XY and Aminopyridine, Hydroxychinoline and Aminopyrazolone.

With this and other well-known Kupplersonstanz the N-Benzylaminophenole forms a broad spectrum of nuances, which is enough from beige to brown violet. The N-Benzylaminophenole according to invention of the formula I is suitable therefore outstanding for the use as oxidation coloring material before products of the type of developer in hair coloring means.

The N-Benzylaminophenole of the formula I can either as such or in form of its salts with inorganic or organic acids, z. B. as hydrochlorides, sulfates, phosphates, acetates, Propionate, Lactate or CIT rate to be isolated and in hair coloring means used.

It is not necessary also that the N-Benzylaminophenole of the formula I represents uniform chemical compounds. Rather these can be also mixtures of different connections of the formula I.

Favorable application characteristics show those Benzylaminophenole of the formula I, in those the two groups of R< 1> and R< 2> Hydrogen are or R< 1> Hydrogen and R< 2> Methyl is and in those up to three of the groups R< 3> to R< 7> a group of OR< 8> and the remaining hydrogen are, whereby R< 8> Hydrogen, an alkyl group with 1-4 C-atoms or a group of hydroxyalkyls with 2-4 C-atoms are.

A set of N-Benzylaminophenolen of the formula I are literature well-known, z. B. of S. Huneck et al., plans Growth regularization, S 75, Springer publishing house (1984).

Not literature well-known a group of N-Benzylaminophenolen of the formula I, which exhibit however particularly favorable application technology characteristics. This new N-Benzylaminophenole of the For I, in which

R< 3> and R< 5> Hydroxy groups are or
 R< 3> , R< 5> and R< 7> Alkoxy groups with 1-4 C-atoms are or
 R< 4> , R< 5> and R< 6> Alkoxy groups with 1-4 C-atoms are or
 R< 4> and R< 6> Alkoxy groups with 1-4 C-atoms are and
 R< 5> a hydroxy group is,
 and the remaining groups of R in each case hydrogen are, are a further the subject of the invention.

When n (2,4-Dihydroxybenzyl) was completely particularly suitable - 4-aminophenol proved, which are characterised apart from its positive toxicological characteristics by the fact that it produces hair colouring, which produced for those regarding color brilliance, chroma and light fastness with 4-Aminophenol as developer component is clearly superior as developer component in oxidation hair coloring means.

This new N-Benzyl-4-aminophenole leaves itself after well-known synthesis processes z. B. manufacture thus that one converts the appropriate 4-Aminophenole of the formula II with the appropriate Benzaldehyd derivatives of the formula III and catalytically hydrogenates the Azomethine of the formula IV formed thereby (in detail regulation in the example part).

EMI5.1

EMI6.1

A further patent article is therefore the procedure for the production of the N-Benzylaminophenole of the formula I, in which R< 3> and R< 5> Hydroxy groups are or

R< 3> , R< 5> and R< 7> Alkoxy groups with 1-4 C-atoms are or
 R< 4> , R< 5> and R< 6> Alkoxy groups with 1-4 C-atoms are or
 R< 4> and R< 6> Alkoxy groups with 1-4 C-atoms are and
 R< 5> a hydroxy group is,
 and the remaining groups of R in each case hydrogen are.

A further patent article are hair coloring means with a content of oxidation coloring material before products into a cosmetic carrier, which contains as oxidation coloring material before products N-Benzylaminophenole of the formula I as developer component in a quantity of 0,05-10 mMol per 100 g of the hair coloring means beside usual Kupplerkomponenten.

For the production of the hair coloring means according to invention the oxidation coloring material before products are trained into a suitable cosmetic carrier. Such carriers are z. B. Creams, emulsions, gels or also tensidhaltige foaming solutions, z. B. Shampoos, foam aerosols or other preparing, which are suitable for applications on the hair.

Usual ingredients of such cosmetic preparing are z. B.:

- Net and emulsifying agents as well as anionische, nichtionische or ampholytische Tenside, z. B. Fat alcohol sulfates, Alkansulfonate, alpha - Olefinsulfonate, Fettalkoholpolyglykolethersulfate
- Products of accumulation of ethyl oxide to Fettalkohole, at fatty acids, at alkyl phenol, at Sorbitanfettsäureester, at Fettsäurepartialglyceride and Fettsäurealkanolamide
- Thickening agent, z. B. Fettalkohole, fatty acids, paraffin oils, fatty acid esters and other fat components in emulsified form
- water-soluble polymere thickening agent, like z. B. Methyl or Hydroxyethylcellulose, strength, Pflanzengumme, water-soluble, synthetic polymers, water-soluble bio polymers (z. B. Xanthan Gum)
- hair-maintaining additives, like z. B. water-soluble kationische polymers, protein derivatives, Pantothenensäure, Vitamine, plant extracts, Cholesterin and sugars
- Electrolyte and buffer salts, pH control agents, complexing agents and perfume oils
- Reducing agents for the stabilization of the coloring material, z. B. Sodium sulfate or ascorbic acid.

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The ingredients of the cosmetic carriers are used for the production of the hair means according to invention into quantities usual for this purpose; z. B. become emulsifying agents in concentrations from 0,5 to 30 Gew. - % and thickening agents in concentrations from 0,1 to 25 Gew. - % of the entire coloring means assigned.

As carriers is particularly suitable a gel with a content from 1 to 20 Gew. -, prefers % of a soap ammonium oleate or an oil in water emulsion with a content from 1 to 25 Gew. - % of a fat component and 0.5 to 30 Gew. - % of an emulsifying agent from the group of the anionischen, nichtionischen, ampholytischen or zwitterionischen Tenside.

The oxidation coloring material before products become in quantities from 0,2 to 5 Gew. - %, preferably 1 to 3 Gew. - %, the entire coloring means into the carrier interfered.

The oxidative development of the colouring can take place in principle with atmospheric oxygen. Preferred however a chemical oxidizing agent is used, particularly if beside the colouring a lightening effect at the hair is wished. As oxidizing agents come in particular hydrogen peroxide or its accumulation products at urea, Melamin or sodium borate as well as mixtures from such products of accumulation of hydrogen peroxide with Kaliumperoxiddisulfat into consideration.

Preferred a preparation of the oxidizing agent is mixed directly before the hair coloring with the preparation from oxidation coloring material before products and carriers. The ready for use hair coloring preparation developing thereby should prefers a pH value within the range of 6 to 10 exhibiting.

The application of the hair coloring means is particularly preferential in a weakly alkaline environment. The application temperatures can lie in a range between 15 and 40 DEG C. After an induction period of approx. 30 minutes the hair coloring means is removed by rinsing out from the hair which can be colored. Washing afterwards with a shampoo is void, if a strongly tensidhaltiger carrier, z. B. a coloring shampoo was used.

The following examples are to describe the invention article more near, without limiting it however on that.

Examples

1. Manufacture examples

Synthesis of n (2,4-Dihydroxybenzyl) - 4-aminophenol: (E1)

11.5 g (0.05 mol) n (2,4-Dihydroxybenzyliden) - 4-aminophenol are taken up to 400 ml ethanol and hydrogenated catalytically with platinum (5% on carbon) as catalyst. After uptake of the computed quantity hydrogen, recrystallized up to dry one eingee is broken off and twice from acetonitrile. Yield: 5.2 g (45%), melting point: 148 DEG C.

Synthesis of n (2,4,6-Trimethoxybenzyl) - 4-aminophenol: (E6)

a) N (2,4,6-Trimethoxybenzyliden) - 4-aminophenol

9.8 g 2,4,6-Trimethoxybenzaldehyd become in approx. 50 ml ethanol solved and filters. 5.4 g 4-Aminophenol one loosens ethanol amine in 300 ml and filters. Under agitating the two solutions are together-given. After short time the product begins to fail. After standing over night one sucks off and one washes with cold ethanol. Yield: 13.8 g (96%), melting point 275 DEG C.

b) N (2,4,6-Trimethoxybenzyl) - 4-aminophenol

11.5 g (0.03 mol) n (2,4,6-Trimethoxybenzyliden) - 4-aminophenol are taken up to 200 ml ethanol and hydrogenated catalytically with platinum (5% on carbon) as catalyst. After uptake of the computed quantity hydrogen is broken off, restricted up to dry one and recrystallized from ethanol. Yield: 7.3 g (84%), melting point: 120 to 122 DEG C.

Synthesis of n (3,4,5-Trimethoxybenzyl) - 4-aminophenol: (E5)

a) N (3,4,5-Trimethoxybenzyliden) - 4-aminophenol

19.6 g 3,4,5-Trimethoxybenzaldehyd become in approx. 50 ml ethanol solved and filters. 10.9 g 4-Aminophenol one loosens ethanol amine in 250 ml and filters. Under agitating the two solutions are together-given. After short time the product begins to fail. After standing over night one sucks off and one recrystallizes from ethanol. Yield: 5.4 g (19%), melting point 187 DEG C.

b) N (3,4,5-Trimethoxybenzyl) - 4-aminophenol

5.4 g (0.019 mol) n (2,4,6-Trimethoxybenzyliden) - 4-aminophenol are taken up to 250 ml ethanol and hydrogenated catalytically with platinum (5% on carbon) as catalyst. After uptake of the computed quantity hydrogen is broken off, restricted and separated the crystallized product. Yield: 4.3 g (79%), melting point: 122 to 126 DEG C.

Synthesis of n (3,5-Dimethoxy-4-hydroxybenzyl) - 4-aminophenol: (E8)

a) N (3,5-Dimethoxy-4-hydroxybenzyliden) - 4-aminophenol

9.1 g 3,5-Dimethoxy-4-hydroxy-benzaldehyd become in approx. 50 ml ethanol solved and filters. 5.4 g 4-Aminophenol one loosens ethanol amine in 50 ml and filters. Under agitating the two solutions are together-given. After short time the product begins to fail.

After standing over night one sucks off and one recrystallizes from ethanol. Yield: 11.9 g (44%), melting point: 208 DEG C.

b) N (3,5-Dimethoxy-4-hydroxybenzyl) - 4-aminophenol

5.4 g (0.02 mol) n (3,5-Dimethoxy-4-hydroxybenzyliden) - 4-aminophenol are taken up to 150 ml ethanol and hydrogenated catalytically with Raney nickel as catalyst. After uptake of the computed quantity hydrogen one breaks off, one restricts and one recrystallizes the jerk from methanol. Yield: 0.5 g (9%), melting point: 153 to 154 DEG C.

2. Sample applications

Hair coloring means according to invention in form of a hair coloring cream emulsion in the following composition were manufactured

< tb> < TABLE> Columns=2>

< tb> Fettalkohol

< tb> Fettalkohol C12 to C14 + 2 EO sulfate, sodium salt 28%ig< SEP> 25 g

< tb> Wasser< SEP> 60 g

< tb> Developer component according to table (1) < SEP> 7,5 mMol

< tb> Kupplerkomponente according to table (1) < SEP> 7,5 mMol

< tb> Na2SO3 (inhibitor) < SEP> 1.0 g

< tb> concentrated Ammoniaklösung< SEP> to pH = 9,5

< tb> Wasser< SEP> ad 100 g

< tb> < /TABLE>

The ingredients were mixed in sequence with one another. After addition of the developer components and the inhibitor first the pH value of the emulsion on 9,5 adjusted became with concentrated ammonia solution, then with water to 100 g one filled up.

The oxidative development of the colouring became with 3%iger hydrogen peroxide solution as oxidation solution conducted. For this wur 100 g of the emulsion with 50 g hydrogen peroxide solution (3%ig) offset and mixes.

The coloring cream became on approx. 5 cm long Strähnen standardized, to 90% did not turn grey however particularly pre-treated people hair laid on and there 30 to minutes with 27 DEG C left. After completion of the dyeing process the hair purged was washed, with a usual Haarwaschmittel and dried afterwards.

As developer components the connections according to invention were used:

```
< tb> < TABLE> Columns=2>
< tb> N (2,4-Dihydroxybenzyl) - 4-aminophenol< CEL
< tb> N (4-Methoxybenzyl) - 4-aminophenol< SEP> E2
< tb> N (2-Hydroxybenzyl) - 4-aminophenol< SEP> E3
< tb> N-Benzyl-4-aminophenol< SEP> E4
< tb> N (3,4,5-Trimethoxybenzyl) - 4-aminophenol< SEP> E5
< tb> N (2,4,6-Trimethoxybenzyl) - 4-aminophenol< SEP> E6
< tb> N (4-Chlorbenzyl) - 4-aminophenol< SEP> E7
< tb> N (3,5-Dimethoxy-4-hydroxybenzyl) - 4-aminophenol< SEP> E8
< tb> < /TABLE>
```

As Kupplerkomponenten the following connections were used:

```
< tb> < TABLE> Columns=2>
< tb> 1-Naphthol< CEL
< tb> 5-Amino-4-chlor-2-methylphenol< SEP> K2
< tb> 1,5-Dihydroxynaphthalin< SEP> K3
< tb> 2,4-Dichlor-3-aminophenol< SEP> K4
< tb> 3-Aminophenol< SEP> K5
< tb> Resorcin< SEP> K6
< tb> 1,3-Bis (2,4-diaminophenoxy) - propan< SEP> K7
< tb> 2-Chlor-3-amino-6-methylphenol< SEP> K8
< tb> 5-Amino-2-methylphenol< SEP> K9
< tb> < /TABLE>
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Table 1 gives an overview of the obtained color nuances of human hair with hair coloring means, which contain N-Benzyl-4-aminophenole as developer components as well as usual Kupplerkomponenten.

Table 1
EMI15.1

N-benzyl-4-aminophenol derivs. as oxidn. dye developers - for human hair, giving strong, bright shades of good fastness**Publication number:** DE4200534**Publication date:** 1993-07-15**Inventor:** KONRAD GUENTHER DR (DE); KNUEBEL GEORG DR (DE); HOEFFKES HORST DR (DE); LIESKE EDGAR (DE)**Applicant:** HENKEL KGAA (DE)**Classification:****- International:** **C07C215/76; C07C217/58; C07C215/00; C07C217/00;**
(IPC1-7): A61K7/13; C07C215/76; C07C217/58;
D06P1/32; D06P3/08**- European:** A61K7/13D; C07C215/76; C07C217/58**Application number:** DE19924200534 19920111**Priority number(s):** DE19924200534 19920111**Report a data error here****Abstract of DE4200534**

Use of N-benzylamino-phenols of formula (I) or their salts as precursors in oxidn. dyeing is new. Where R1-R7 = H or 1-4C alkyl; up to 3 of R3-R7 can also be Cl or OR8 and the other R gps. H; R8 = H, 1-4C alkyl or 2-4C hydroxyalkyl. (I) and their salts are new where (a) R3 = R5 = H; (b) R3, R5 and R7 = 1-4C alkoxy; (c) R4, R5 and R6 = 1-4C alkoxy; or (d) R4 and R6 = 1-4C alkoxy and R5 = OH, th eother R gps. being H. Pref. deriv. of (I) is N-(2,4-dihydroxybenzyl)-4-aminophenol. USE/ADVANTAGE - (I) are developers for dyeing keratin fibres, esp. human hair. When used with a wide variety of usual couplers they provide bright shades (beige to brown-violet) of good fastness properties. Partic. they give shades of better brightness, colour depth and light fastness than 4-aminophenol itself.

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